Supporting Information

Electrocatalysis of CO_2 Reduction in Brush Polymer Ion Gels

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Materials and Methods Section:

General

Pentacarbonylrhenium(I) chloride (Sigma-Aldrich), 2,2'-bipyridyl (Sigma-Aldrich). 1,3-butylmethylimidazolium bis(trifluoromethylsulfonyl)imide, 1,3-ethylmethylimidazolium ethylsulfate, and 1,3-ethylmethylimidazolium triflate (Iolitec, Inc.) were dried under vacuum at 65 degrees Celsius for 24 hours prior to use. Anhydrous DCM was used for all syntheses. $Re(bpy)(CO)_3Cl$ was prepared according to literature precedent.[1] Polystyrene and polyethyleneoxide macromonomers were synthesized according to literature precedent using atom transfer radical polymerization.[2]

15:119:15 Polystyrene-polyethyleneoxide-polystyrene (PS:PEO:PS) brush-block copolymer. Using polystyrene and polyethyleneoxide macromonomers and Grubbs 3rd generation catalyst, shown in **Figure S1**, PS:PEO:PS was synthesized according to literature precedent.[2,3] Under inert atmosphere, the macromonomers and catalyst were dissolved separately in anhydrous DCM. The vials contained PS macromonomer (15.0 eq., 0.953 g), DCM (4.52 mL); PEO macromonomer (120.0 eq., 6.831 g), DCM (40 mL); PS macromonomer (15.0 eq., 0.953 g), DCM (5.0 mL). A DCM (1.244 mL) solution of the catalyst was also prepared (0.025 mmol). Polymerization was initiated by injecting an aliquot of the catalyst solution (0.726 mL) into the first PS macromonomer solution. After 40 minutes, the PEO macromonomer solution was added to the first reaction. After 100 min, the second PS macromonomer solution was added to the reaction mixture. After 120 min, the solution was stirred and quenched with ethyl vinyl ether (5 mL) outside of the glovebox. Before addition of each block, an aliquot of the reaction was quenched with ethyl vinyl ether for characterization by SEC. The polymer was precipitated using diethyl ether at -78 °C. The precipitate was filtered and dried *in vacuo*. Size exclusion chromatography in THF with 1 % triethylamine by volume and ^1H NMR were used to calculate dispersity indices and average molecular weights of polymerized PS, PS:PEO, and PS:PEO:PS which are summarized in **Table S1**. This polymer has also been previously characterized by small-angle X-ray scattering, differential scanning calorimetry (DSC), and AC impedance spectroscopy.[2]

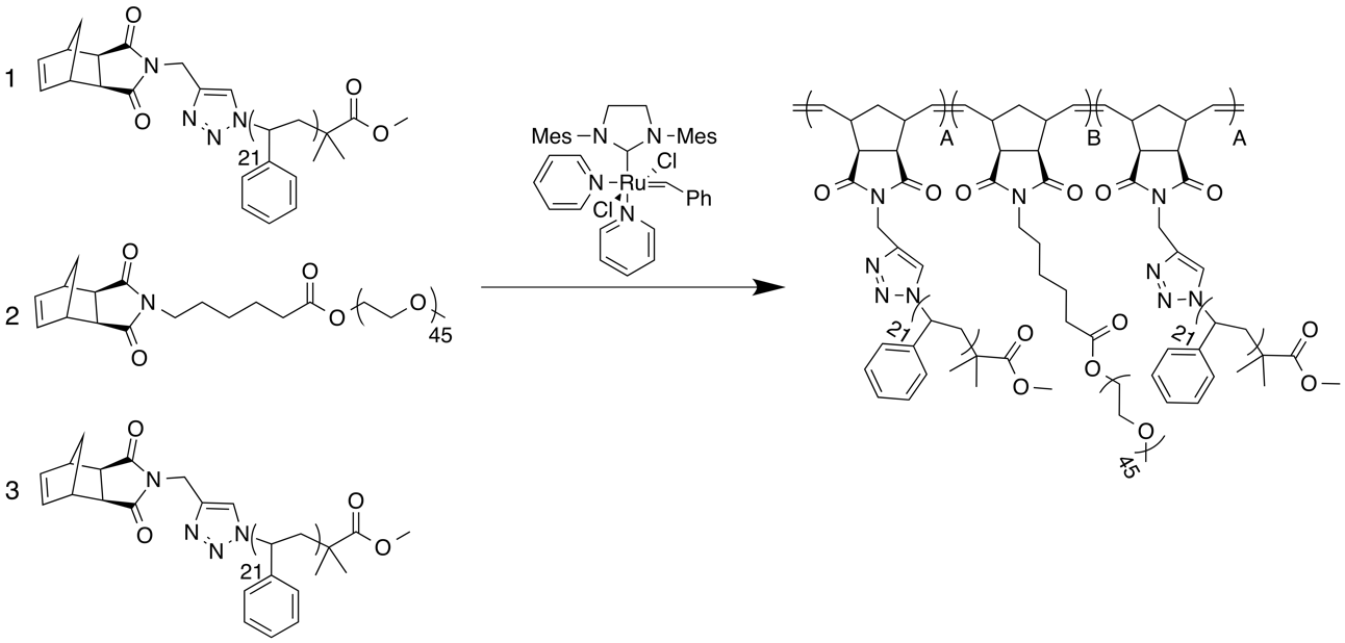

Figure S1. Macromonomers and general structure of PS:PEO:PS after polymerization with Grubbs 3rd generation catalyst.

Sample	N	M_n (kDa)	M_w (kDa)	$Đ$
PS_{15}	15	38.41	38.55	1.00
PS_{15}-PEO_{119}	15-119	562.6	604.2	1.07
PS_{15}-PEO_{119}-PS_{15}	15-119-15	710.0	769.3	1.08

Table S1. The degrees of polymerization (N) were calculated from SEC and ^{1}H NMR. All other parameters were calculated from SEC. This data has been previously reported.[2]

15:119:15 PS:PEO:PS-BMIm-TFSI. In a glove box atmosphere, 15:119:15 polystyrene-polyethyleneoxide-polystyrene (100. mg) was dissolved in anhydrous dichloromethane (1.0 mL) and stirred for ten minutes. Additional dichloromethane (1.0 mL) and 1,3-butylmethylimidazolium bis(trifluoromethylsulfonyl)imide (0.70 mL) were added, and the mixture was stirred for an additional ten minutes. Ferrocene, cobaltocenium hexafluorophosphate, and Re(bpy)$(CO)_3$Cl were added after the polymer was dissolved in ionic liquid and DCM. The stir bar was removed from the reaction, and the solution was allowed to sit for 36 hours to evaporate the dichloromethane and cast the gel electrolyte. Gels were confirmed to be free of DCM by ^{1}H NMR. Characterization of the ion gel with these specific degrees of polymerization has been previously reported in publications from our groups, including small-angle X-ray scattering, differential scanning calorimetry, dynamic mechanical analysis, and AC impedance spectroscopy.[3] Gels with 9 % by weight 15:119:15 PS:PEO:PS exhibit a glass transition temperature (T_g) equal to -81 ^{o}C and an ionic conductivity equal to 2 mS cm^{-1}.[3]

Electrochemical Measurements:
All electrochemical characterization of ionic liquid-polymer gel electrolytes was performed in an inert, argon atmosphere. Electrochemical characterization of ionic liquids was performed with a Gamry Reference 600 or Bio-Logic VSP-300 potentiostat by transferring dried ionic liquid into a nitrogen-purged standard three-electrode cell containing a 3 mm diameter glassy carbon electrode (CH Instruments) working electrode, silver wire pseudo-reference electrode (CH Instruments), and platinum wire counter electrode (Kurt J. Lesker). Bulk electrolysis measurements were performed in a gas-tight cell with a glassy carbon plate with a 1.35 cm^2 working area, a 0.01 M $Ag^{+/0}$ quasireference electrode (BMIm-TFSI) or Ag wire pseudoreference electrode (ion gel), and a platinum mesh counter electrode separated by a glass frit. The cell was purged with CO_2 for 2 hours prior to being sealed. Prior to gel electrolysis, gels were vacuum-dried for 4 days. Ultramicroelectrode experiments were performed with an 11 μm carbon fiber disk electrode, Ag pseudoreference electrode, and platinum wire counter electrode. All macrodisk and electrolysis experiments were compensated for 80-85% of the measured uncompensated resistance (R_u) value.

Gas Chromatography:
After 1 hour of electrolysis, 10 mL of headspace were sampled with a gas-tight syringe and injected into an Agilent 7890a gas chromatograph. A calibration curve was obtained using mixtures of different percent volumes of CO in CO_2. For experiments with BMIm-TFSI, the headspace was measured to be 52.5 mL. For ion gel experiments, the headspace was measured to be 62 mL.

Small Angle X-Ray Scattering (SAXS) of Ion Gels:

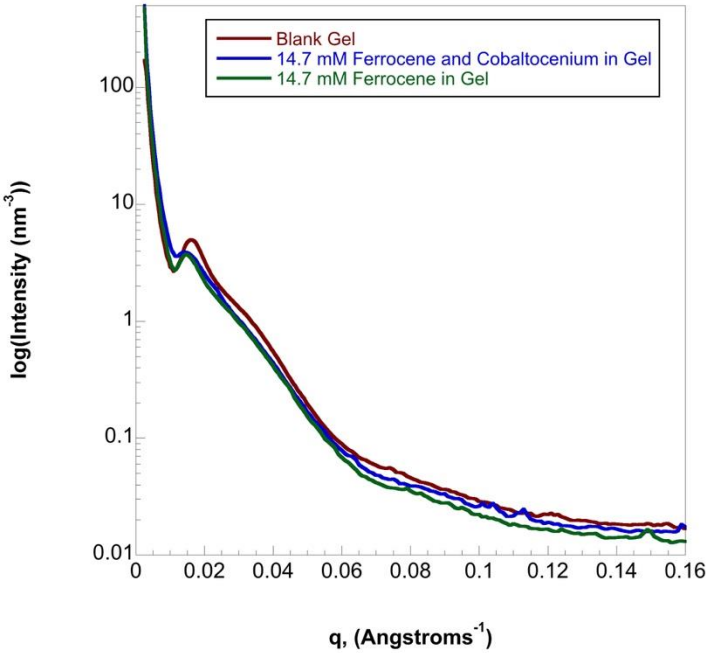

Figure S2. Small Angle X-Ray Scattering (SAXS) of ion gels containing various electroactive molecule loadings. These data are consistent with a network of disordered spherical micelles; see our previous report for detailed brush polymer ion gel SAXS characterization and data analysis.[3]

Nicholson and Shain Metrics for Fc^+/Fc:

To calculate peak current ratios, the baselines were manually drawn and subtracted or added from the observed peak currents. Due to the large uncompensated resistance of ion gels, a distortion of the voltammetric wave towards larger peak-to-peak separation occurs. This distortion means that the only reliable metric is the peak current ratio versus scan rate, shown below for the three samples with ferrocene.

Peak Current Ratio versus Logarithm of the Scan Rate:

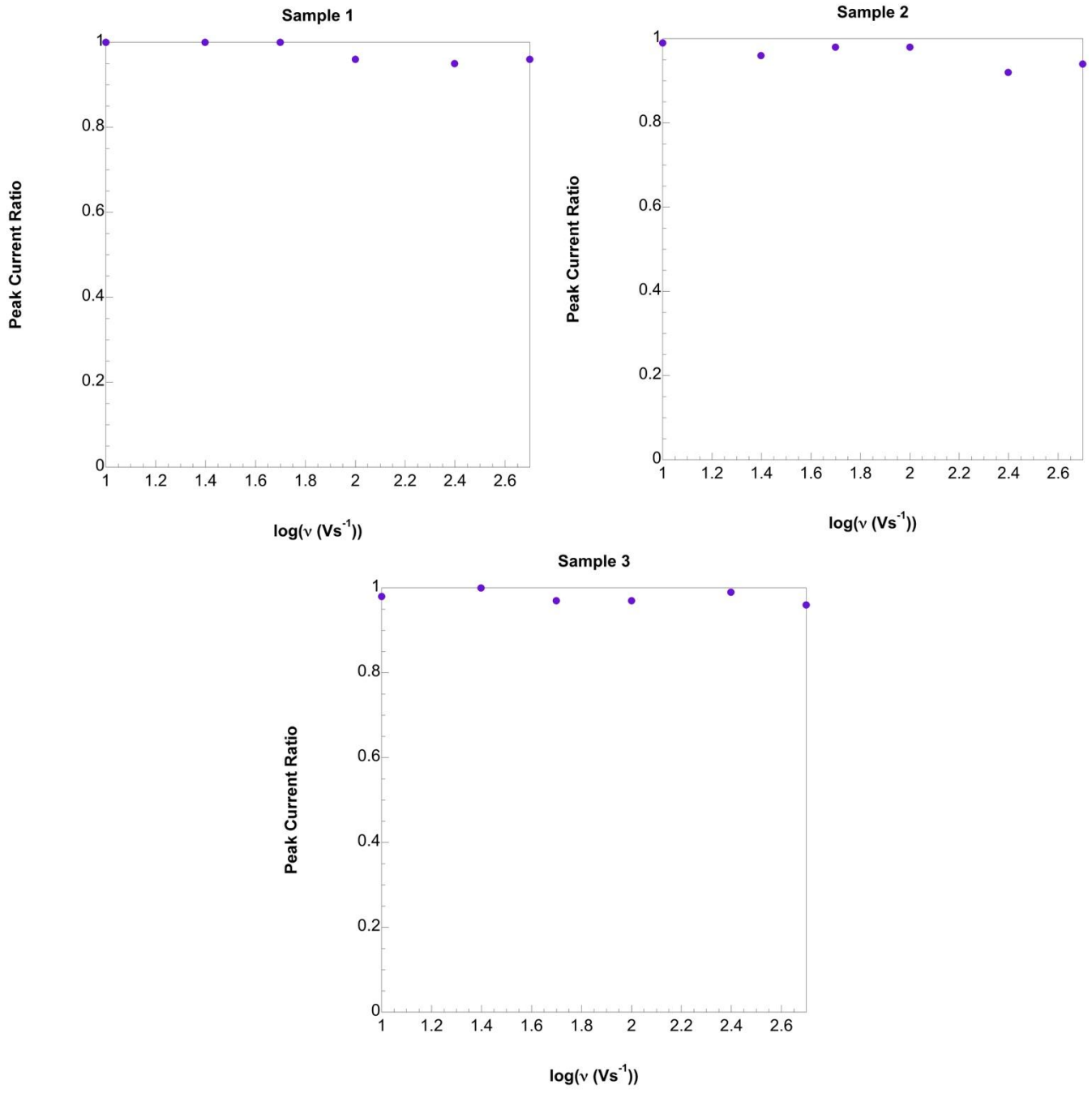

Figure S3. The peak current ratio for all samples is nearly constant at all scan rates, indicating that the redox mechanism of ferrocene in ionic liquid-polymer gel electrolytes is a reversible, single electron transfer.

Scan Rate Dependence and Randles-Sevcik Plots for $Fc^{+/0}$

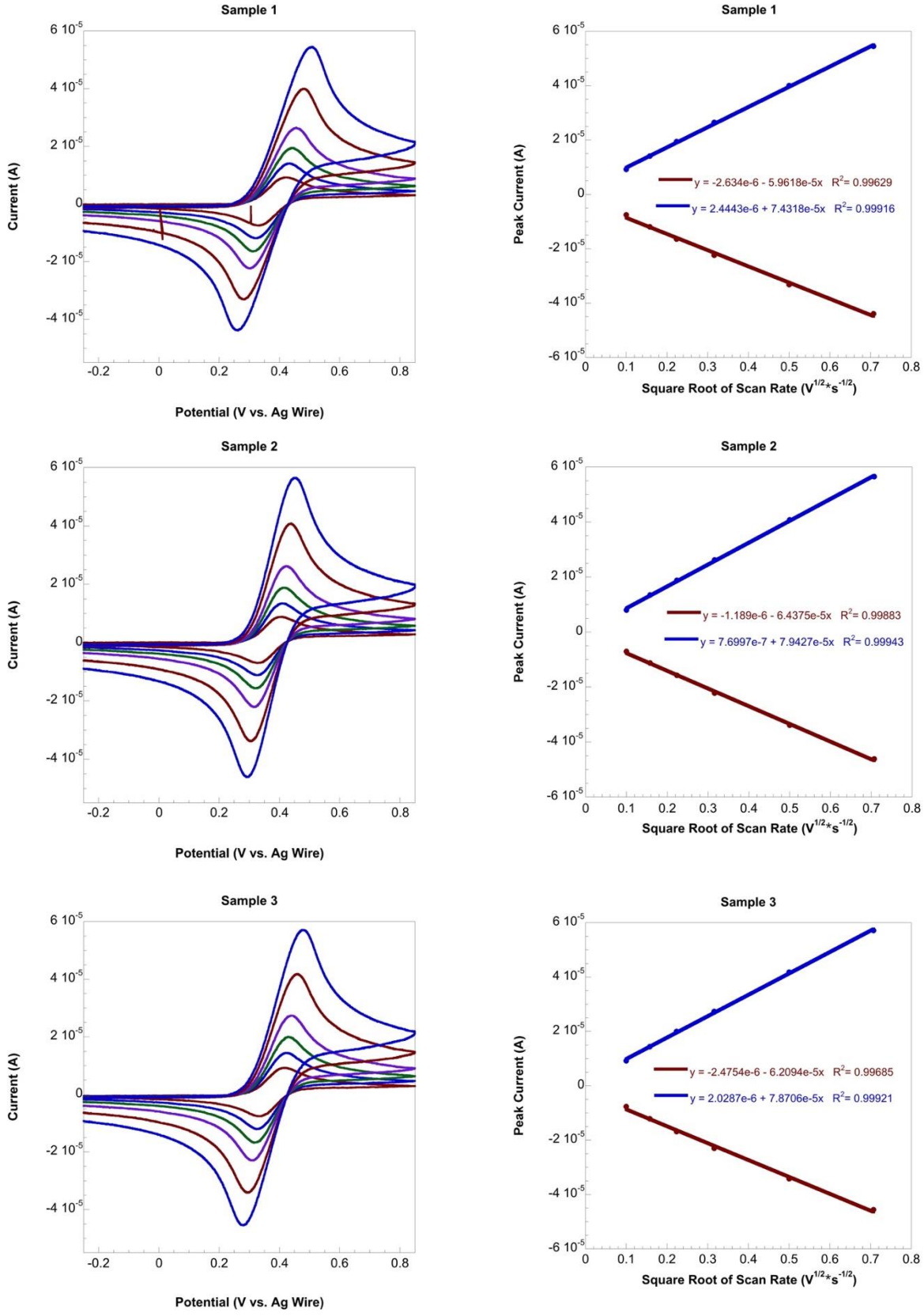

Figure S4. Scan rate dependence for 14.7 mM ferrocene in ion gel electrolyte

Scan Rate Dependence and Randles-Sevcik Plots for $CoCp_2^{+/0}$

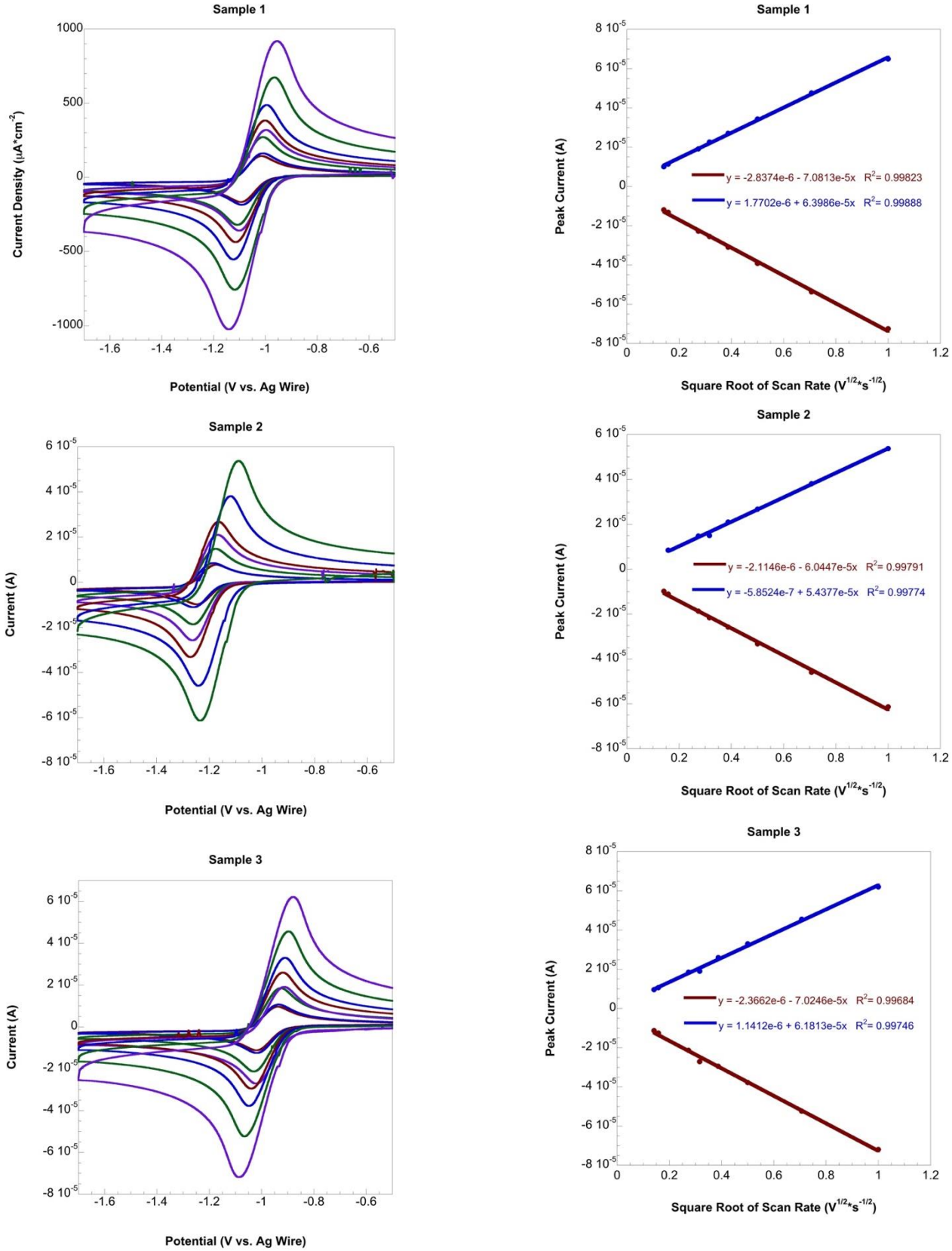

Figure S5. Scan rate dependence for 14.7 mM $[CoCp_2]PF_6$ in ion gel electrolyte.

Microelectrode (ME) electrochemistry of $Re(bpy)(CO)_3Cl$ in BMIm-TFSI without and with CO_2:

To determine more information about the number of electrons transferred and confirm the mechanism of catalysis observed at a macrodisk electrode, ME electrochemistry of $Re(bpy)(CO)_3Cl$ was performed with an 11 micrometer carbon fiber disk micro working electrode. **Figure S6** displays the steady-state voltammetry observed, and three separate redox processes are visible. **Table S2** gives corrected limiting current values and the estimated potential reached at steady state obtained from this plot.

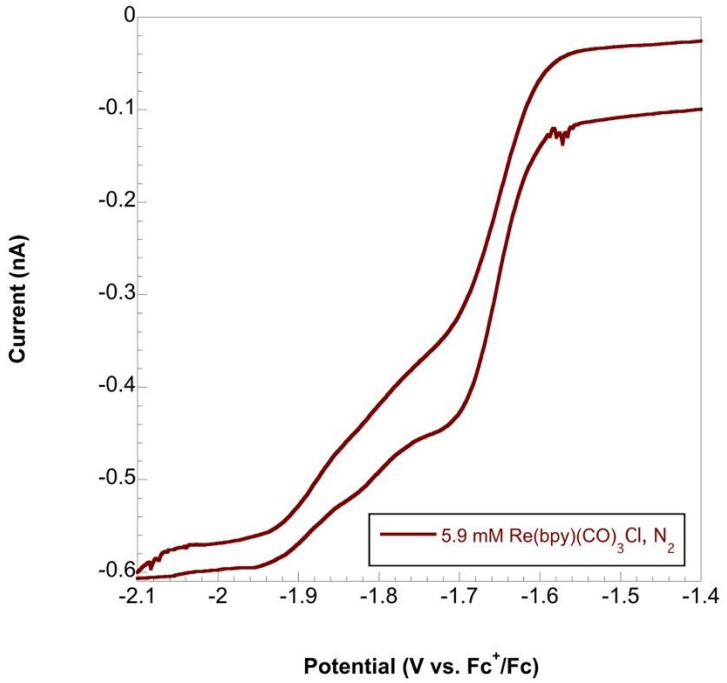

Figure S6. Cyclic voltammetry of 5.9 mM $Re(bpy)(CO)_3Cl$ in BMIm-TFSI.

Redox Process	Potential at $i_{1/2}$ (V vs. $Fc^{+/0}$)	Peak Cathodic Potential at 3 mm Diameter GC (V vs. $Fc^{+/0}$)	Current at Steady State (pA)
1	-1.66	-1.67	-243.2
2	-1.82	-1.83	-44.6
3	-1.91	-1.91	-35.0

Table S2. Cyclic voltammetry of 5.9 mM $Re(bpy)(CO)_3Cl$ in BMIm-TFSI. Current values were corrected using blank CV at 10 mV s^{-1}.

The values obtained at $E_{1/2}$ in UME experiments correlate well with the values obtained in macrodisk experiments. **Equation 1** gives the steady state current associated with a disk UME, where C_0 is the bulk concentration of the electroactive species and r is the radius of the microdisk electrode.

$$i_{ss} = 4nFDC_0r_0 \quad \textbf{(1)}$$

Using the above equation, a steady state reduction current in BMIm-TFSI for a one-electron process with a diffusion coefficient of 10^{-7} cm^2s^{-1} is -0.126 nA.[4] Based on the currents obtained for the three redox processes, approximately two electrons are transferred for the first reduction, and the other two waves most likely correspond to two consecutive reductions of the same species present in a smaller concentration. These data contrast with a previous report studying a non-coordinating anion that

generates a single reduction wave.[5] Collectively, these observations support the interpretation that ligand exchange is the underlying cause of multiple reduction processes, which is more probable for the complex in ionic liquid with a stronger coordinating anion. If the total current is used to find the diffusion coefficient for a two-electron transfer to all electroactive species, $D = 1.8 \times 10^{-11}$ m^2 s^{-1}, which correlates well with the coefficient obtained in macrodisk experiments.

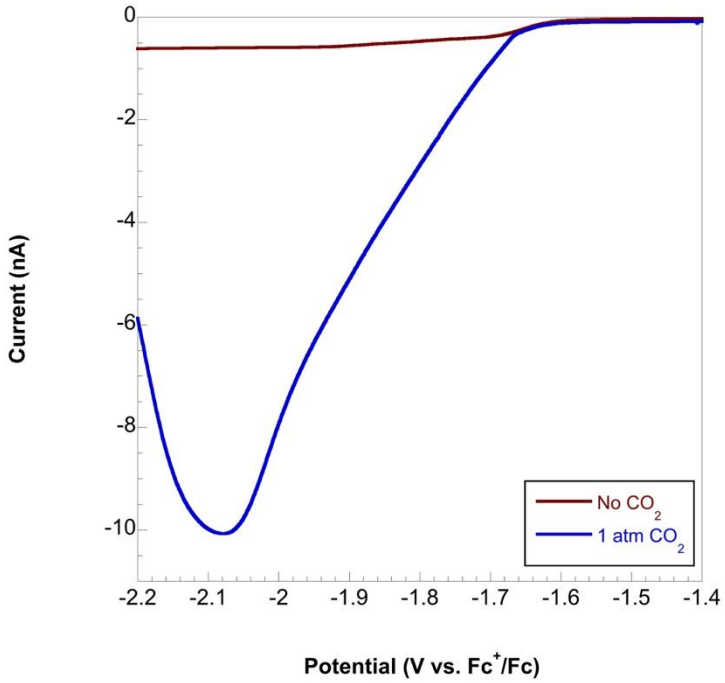

Figure S7. Cyclic voltammetry of 5.9 mM Re(bpy)(CO)$_3$Cl in BMIm-TFSI under 1 atm CO_2. The working electrode was an 11 micrometer diameter carbon fiber disk microelectrode.

Figure S7 gives the current response of the system in the absence and in the presence of CO_2, with a large catalytic wave peaking at -2.08 V vs. Fc^+/Fc. Since a change in the slope of the current response occurs over the course of catalysis, the two analogues of the catalyst present in solution are both catalytically active. Adding together the currents of all redox processes in the absence of CO_2 gives a total current of -0.314 nA. The peak current ratio, i_{cat}/i_{ss}, is equal to 30.8, which agrees with the ratio of 29.9 obtained at 10 mVs^{-1} in the macrodisk experiment.

Cyclic Voltammetry of $Co(tpfc)(py)_2$ in BMIm-TFSI at 100 mVs^{-1}:

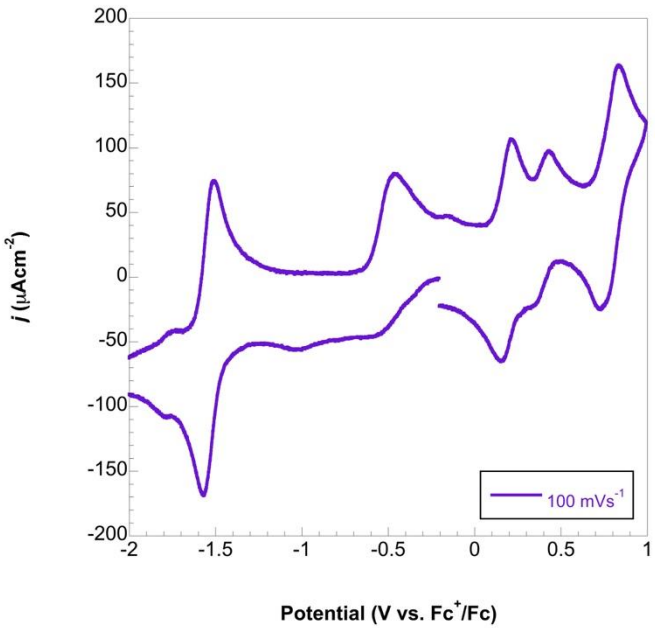

Figure S8. Voltammetry of $Co(tpfc)(py)_2$ in BMIm-TFSI. The voltammetry implies two active forms of the complex, with double the redox events typically observed in nonaqueous solvents.

Randles-Sevcik Plot for $Re(bpy)(CO)_3Cl$ in BMIm-TFSI:

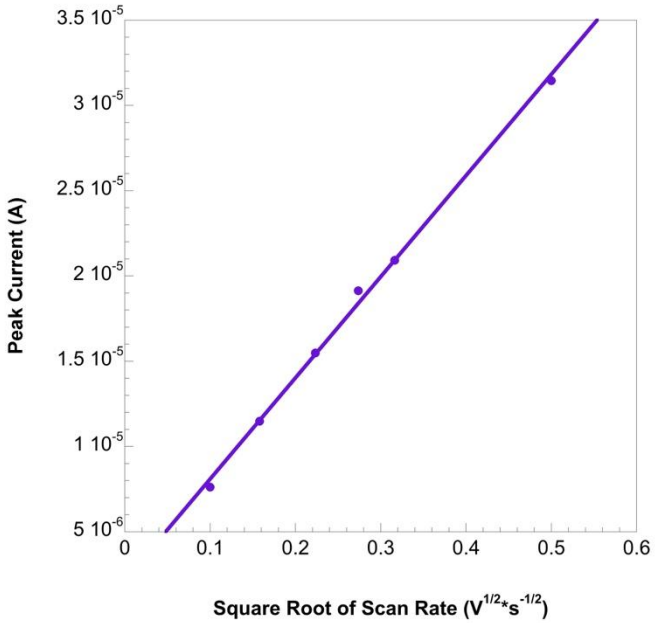

Figure S9. The linear dependence on the square root of the scan rate for the first reduction of $Re(bpy)(CO)_3Cl$ in BMIm-TFSI suggests a diffusion-controlled process, which means an accurate measure of the diffusion coefficient of the complex can be made. The plot does not indicate whether or not the reaction is electrochemically reversible.

Bulk Electrolysis of $Re(bpy)(CO)_3Cl$ in BMIm-TFSI:

To compare the Faradaic efficiency obtained for CO production between neat BMIm-TFSI and ionic liquid-polymer gel electrolyte, chronoamperometry of a solution of 1.6 mM $Re(bpy)(CO)_3Cl$ in BmIM-TFSI was carried out for 1 hour.

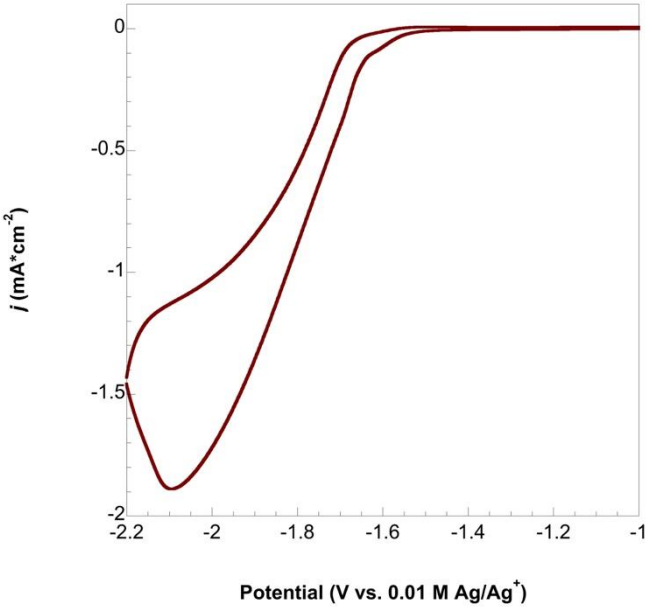

Figure S10. Cyclic voltammetry of 1.0 mM $Re(bpy)(CO)_3Cl$ in CO_2-saturated BMIm-TFSI. Ferrocene was added at the end of electrolysis as an internal reference.

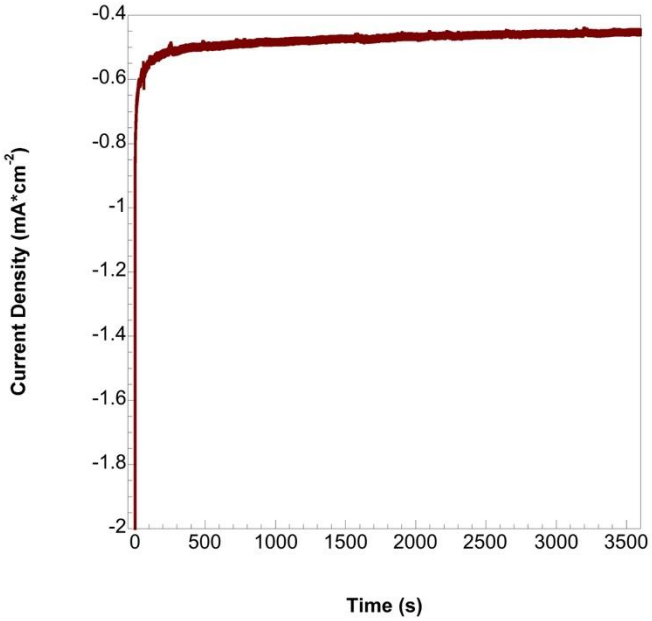

Figure S11. 1 hour controlled-potential electrolysis of 1.6 mM $Re(bpy)(CO)_3Cl$ in CO_2-saturated BMIm-TFSI. A 10 mL aliquot of headspace was taken after electrolysis. A total of 2.414 C was passed in 1 hour.

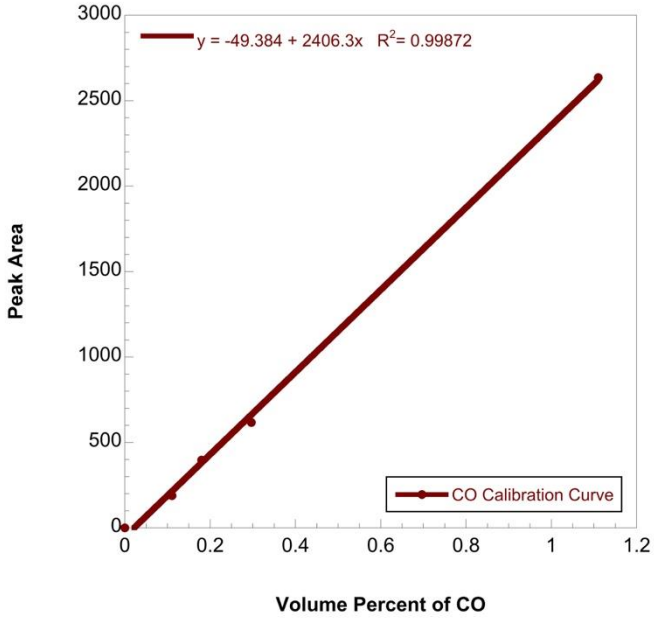

Figure S12. Gas chromatograph calibration curve for carbon monoxide.

Based on the calibration curve for CO, the Faradaic efficiency for this trial for the production of CO was 94.2%, a slightly improved Faradaic efficiency over that found in EMIm-TCB.[5]

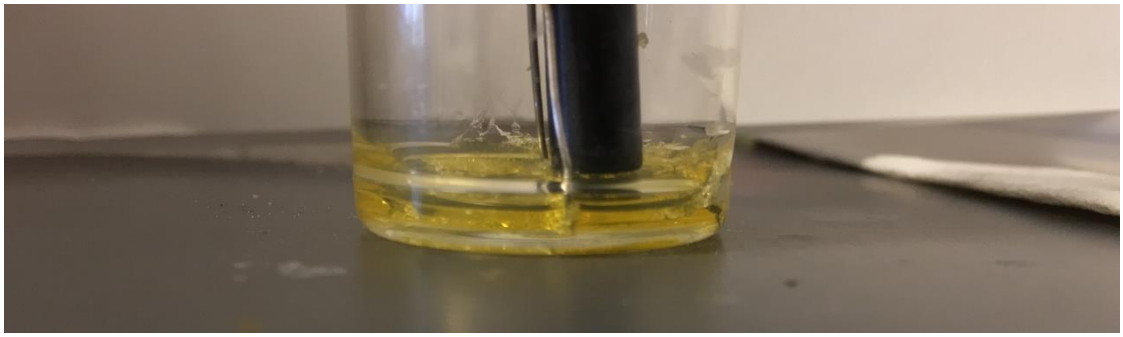

Figure S13. Working electrode resting vertically on a polymer ion gel and counter and reference electrodes inserted into the gel. The gel deforms slightly when wires are inserted.

References:

(1) Smieja, J. M.; Kubiak, C. P. *Inorg. Chem.* **2010**, *49*, 9283.

(2) Bates, C. M.; Chang, A. B.; Momčilović, N.; Jones, S. C. *Macromolecules* **2015**, *48*, 4967.

(3) Bates, C. M.; Chang, A. B.; Schulze, M. W.; Momcilovic, N.; Jones, S. C.; Grubbs, R. H. *J. Polym. Sci. B Polym. Phys.* **2016**, *54*, 292.

(4) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley, 2000.

(5) Grills, D. C.; Matsubara, Y.; Kuwahara, Y.; Golisz, S. R.; Kurtz, D. A.; Mello, B. A. *J. Phys. Chem. Lett.* **2014**, *5*, 2033.